

## Response of surface water chemistry to reduced levels of acid precipitation: comparison of trends in two regions of New York, USA

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### Abstract:

In light of recent reductions in sulphur (S) and nitrogen (N) emissions mandated by Title IV of the *Clean Air Act Amendments* of 1990, temporal trends and trend coherence in precipitation (1984–2001 and 1992–2001) and surface water chemistry (1992–2001) were determined in two of the most acid-sensitive regions of North America, i.e. the Catskill and Adirondack Mountains of New York. Precipitation chemistry data from six sites located near these regions showed decreasing sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), and base cation ( $\text{C}_B$ ) concentrations and increasing pH during 1984–2001, but few significant trends during 1992–2001. Data from five Catskill streams and 12 Adirondack lakes showed decreasing trends in  $\text{SO}_4^{2-}$  concentrations at all sites, and decreasing trends in  $\text{NO}_3^-$ ,  $\text{C}_B$ , and  $\text{H}^+$  concentrations and increasing trends in dissolved organic carbon at most sites. In contrast, acid-neutralizing capacity (ANC) increased significantly at only about half the Adirondack lakes and in one of the Catskill streams. Flow correction prior to trend analysis did not change any trend directions and had little effect on  $\text{SO}_4^{2-}$  trends, but it caused several significant non-flow-corrected trends in  $\text{NO}_3^-$  and ANC to become non-significant, suggesting that trend results for flow-sensitive constituents are affected by flow-related climate variation.  $\text{SO}_4^{2-}$  concentrations showed high temporal coherence in precipitation, surface waters, and in precipitation–surface water comparisons, reflecting a strong link between S emissions, precipitation  $\text{SO}_4^{2-}$  concentrations, and the processes that affect S cycling within these regions.  $\text{NO}_3^-$  and  $\text{H}^+$  concentrations and ANC generally showed weak coherence, especially in surface waters and in precipitation–surface water comparisons, indicating that variation in local-scale processes driven by factors such as climate are affecting trends in acid–base chemistry in these two regions. Copyright © 2005 John Wiley & Sons, Ltd.

**KEY WORDS** acid precipitation; surface water chemistry; trends; sulphate; nitrate; ANC; DOC; Catskills; Adirondacks; New York

### INTRODUCTION

Atmospheric acid deposition is widespread in North America, Europe, and Asia (Rodhe *et al.*, 2002), and an array of environmental effects have been attributed to acidic deposition, including (1) acidification of sensitive surface waters, (2) toxicity to aquatic biota, and (3) toxicity and growth limitation in terrestrial vegetation (Schindler, 1988; Havens *et al.*, 1993; Driscoll *et al.*, 2001). The Adirondack and Catskill Mountains of New York are two regions of the northeastern USA that contain an abundance of waters with low acid-neutralizing capacity (ANC) whose watersheds are sensitive to the effects of acid deposition (Omernik and Powers, 1983; Brakke *et al.*, 1988). This sensitivity arises from relatively high rates of acid deposition imposed on landscapes that consist of steep slopes and thin till and soil cover, with slow rates of bedrock weathering and a short growing season. In particular, many lakes in the western Adirondacks and streams in the Neversink River and Rondout Creek watersheds of the Catskills have been acidified by acid deposition (Driscoll *et al.*, 1991; Stoddard and Murdoch, 1991). The biological effects of acid deposition in these regions include loss of

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acid-sensitive aquatic species, such as brook trout, minnows, and mayflies (Baker and Christensen, 1991; Baker *et al.*, 1993; Baldigo and Lawrence, 2000), as well as possible induced stress and (or) decline of red spruce and sugar maple (Shortle *et al.*, 1997; Horsley *et al.*, 2002).

During the past two decades, however, the acidity of precipitation has declined over large portions of eastern North America and western Europe, including the Adirondack and Catskill Mountain regions (Stoddard *et al.*, 1999; Lynch *et al.*, 2000), due to more stringent air pollution emission laws, the widespread availability of improved pollutant removal technologies, and energy conservation. The goal of these acid-deposition-related emission laws, such as the *Clean Air Act Amendments* of 1990 in the USA and the 1994 Oslo Protocol in Europe, are to reduce the acidity of precipitation and allow the chemical and biological recovery of previously impacted waters and ecosystems. Analyses of monitoring data in eastern North America dating to the mid-1990s generally indicated decreased sulphate ( $\text{SO}_4^{2-}$ ) concentrations in surface waters in parallel with decreased  $\text{SO}_4^{2-}$  concentrations in precipitation, but little decrease in nitrate ( $\text{NO}_3^-$ ) concentrations, and only slight increases or no change in pH and ANC (Burns *et al.*, 1998; Driscoll *et al.*, 1998; Stoddard *et al.*, 1999; Watt *et al.*, 2000; Clair *et al.*, 2002). More recent analyses of recovery-related trends have generally found more widespread and significant changes in chemistry, with sharper decreases in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations and increases in pH and ANC (Evans *et al.*, 2001; Driscoll *et al.*, 2003; Kahl *et al.*, 2004). These widespread trends toward recovery have also become evident in the Adirondack and Catskill Mountain regions (Driscoll *et al.*, 2003; Kahl *et al.*, 2004). Despite these encouraging trends, there has been no convincing evidence of recovery in surface water chemistry sufficient to promote widespread biological recovery (Watt *et al.*, 2000).

The research effort to date on recovery of surface waters from reduced levels of acid precipitation has used mainly long-term chemistry data sets with no correction for hydrologic conditions, which reflect patterns in climatic conditions (Driscoll *et al.*, 1998, 2003; Stoddard *et al.*, 1999; Kahl *et al.*, 2004). Climate variation that affects flow conditions may have large effects on the concentrations of flow-sensitive ionic species such as  $\text{NO}_3^-$  and ANC that can affect trend analysis (Lawrence *et al.*, 2004). Here, we compare temporal trends in chemical constituents with and without correcting for flow effects. Additionally, continued effort is needed to document (1) the relation of trends in the chemistry of precipitation to those of surface water chemistry within a region, and (2) either synchronicity or the lack thereof of surface water chemistry trends across regions that may be experiencing similar declines in the acidity of precipitation. The presence or lack of synchronicity may demonstrate whether the biogeochemical processes governing recovery appear to operate at the scale of individual watersheds or are more widespread across regional scales (Stoddard *et al.*, 1998). Here, we explore trends in precipitation and surface water chemistry from 1992 to 2001 within and across the acid-deposition-sensitive Adirondack and Catskill regions of New York. We also examine spatial variability of the synchronicity of temporal trends to determine if these two regions are responding similarly to recent declines in the acidity of precipitation.

## STUDY SITE

The study regions are within the Adirondack and Catskill Parks in New York (Figure 1). The Adirondack Park consists of  $2.4 \times 10^6$  ha of predominantly forested land in northern New York, and is the largest publicly protected area in the contiguous USA. The Adirondacks contain an estimated 1290 lakes with surface areas  $>4$  ha (Brakke *et al.*, 1988), and also abundant wetlands, streams, and smaller lakes. There is wide variability in the landscape and climate across the Adirondacks, but the region is generally underlain by granitic gneiss and metasedimentary rock with acidic Spodic soils developed in glacial till that is 12 000 to 18 000 years old (Driscoll *et al.*, 1991). The climate is described as humid continental, with short cool summers and long cold winters (Trewartha, 1954). A recent analysis of temperature (15 sites) and precipitation (24 sites) data from the Adirondacks found a mean annual precipitation amount of 105.4 cm and mean annual air temperature of  $6.3^\circ\text{C}$  (Ito *et al.*, 2002). Snowfall accounted for 31% of total precipitation in the early 1980s in the western Adirondacks, where most of the study lakes are located (Johannes *et al.*, 1985).

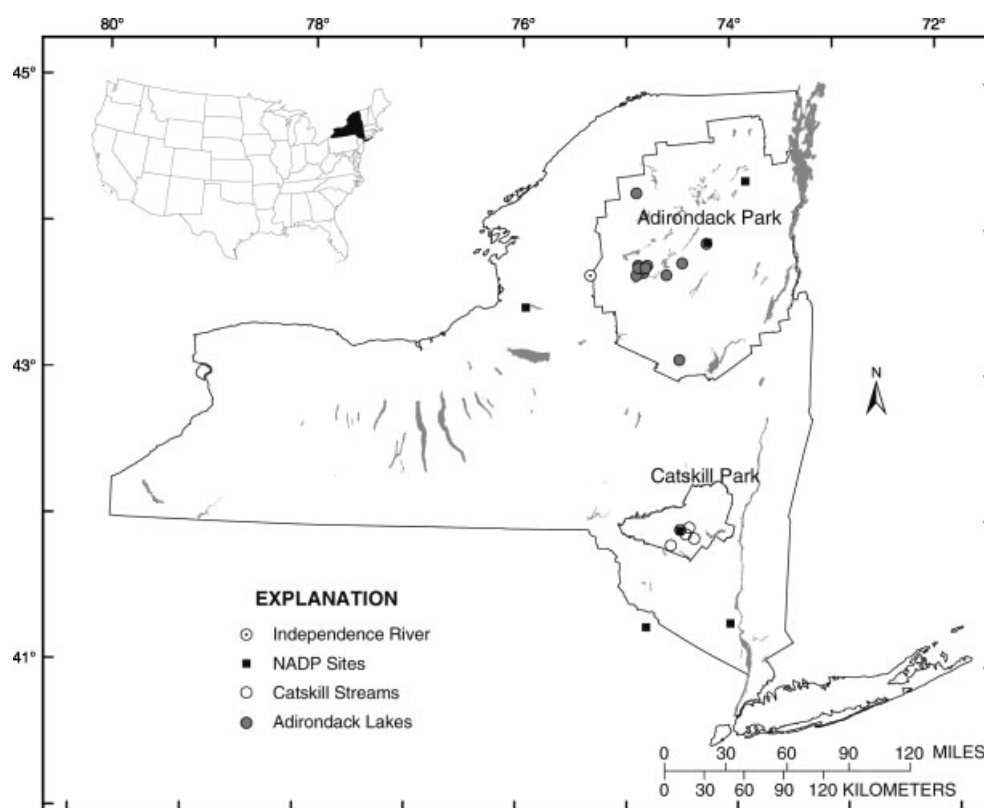


Figure 1. Map of study regions showing locations of surface water and precipitation sampling sites within or near the Adirondack and Catskill Parks in New York, USA. The Independence River gauge used as an index of flow in the Adirondack lakes is also shown

The Catskill Park consists of  $2.4 \times 10^5$  ha of predominantly forested land in southeastern New York. The Catskills are a raised plateau of sedimentary rock that has been dissected by streams and rivers; lakes in the region are much less numerous than in the Adirondacks. The Neversink River and Rondout Creek basins that are the focus of this investigation are largely underlain by sandstone and conglomerate with some interbedded shale. Soils in the region are generally Inceptisols that have developed in glacial till that is of a similar age to that in the Adirondacks, and the climate is also similar to that of the Adirondacks (Stoddard and Murdoch, 1991). Mean annual temperature and precipitation are  $4.6^\circ\text{C}$  and 153 cm respectively at the Slide Mountain weather station at 808 m elevation in the headwaters of the Neversink River basin (Burns and Murdoch, 2005), and 20–25% of precipitation consists of snowfall at this site. Mean annual air temperature in the western Adirondacks is comparable to that of the Slide Mountain site; however, the western Adirondacks have slightly lower precipitation amounts of 120–130 cm (Ito *et al.*, 2002). Levels of atmospheric nitrogen (N) deposition, which are driven foremost by precipitation amount, are similar in the Catskills and western Adirondacks (Ollinger *et al.*, 1993).

## METHODS

### *Precipitation chemistry*

Precipitation chemistry data from six sites were analysed: three sites from the Adirondack region and three sites from the Catskill region (Table I). These sites are monitored as part of the National Atmospheric Deposition Program (NADP; <http://nadp.sws.uiuc.edu>). The sites chosen for analysis were the six in the NADP

Table I. Description, identification, elevation, location, and length of record of NADP precipitation chemistry sites analysed in this study

Site ID	Description	Elevation (m)	Lat. (N)	Long. (W)	Length of record
<i>Adirondacks</i>					
NY52	Bennett Bridge	245	43.5261	75.9472	10 June 1980–present
NY20	Huntington Wildlife	500	43.9731	74.2231	31 October 1978–present
NY98	Whiteface Mountain	610	44.3933	73.8594	3 July 1984–present
<i>Catskills</i>					
NY68	Biscuit Brook	634	41.9942	74.5036	11 October 1983–present
NY99	West Point	201	41.3508	74.0486	13 September 1983–present
PA72	Milford	212	41.3275	74.8203	27 December 1983–present

network that were closest to these two regions and had data records of sufficient length to encompass the study period (1980s to present).

Samples of wet deposition are collected weekly at each site from a wet–dry collector and shipped to the NADP laboratory in Champaign, Illinois, for analysis. Sample handling, analytical methods and quality assurance (QA) procedures are described on the NADP Website at <http://nadp.sws.uiuc.edu/QA>.

#### *Surface water chemistry*

Site selection was limited by the availability of long-term stream chemistry data of sufficient length ( $\geq 10$  years) and intensity of sample collection with minimal influence from on-the-ground human activities. Thus, data from just five sites in the Catskills were analysed in this study: Biscuit Brook, Rondout Creek, West Branch Neversink River at Winnisook, East Branch Neversink River at Tison, and Neversink River at Claryville. These sites were not chosen in a random manner to represent the Catskills as a whole statistically, an approach used in many monitoring networks designed to detect trends (Stoddard *et al.*, 1996; Urquhart *et al.*, 1998). Rather, these five sites are located in the two Catskill watersheds that contain streams with the lowest ANC, which are believed to be among the most sensitive to acidification within the Catskill region (Stoddard and Murdoch, 1991). Four of these five stream sites were used by the US Environmental Protection Agency in past trend analyses to represent the northern Appalachian Plateau geomorphic province (Stoddard *et al.*, 1999, 2003).

Site selection in the Adirondacks was from a population of 52 lakes that are part of the Adirondack Long-Term Monitoring (ALTM) Program operated by the Adirondack Lakes Survey Corporation. These lakes have been sampled monthly since 1992, and some have been sampled since 1982. Because available chemical data for the Catskills were from streams, we attempted to find the most stream-like data from among the ALTM lakes. Previous research has found that within-lake biological processes, such as denitrification and  $\text{SO}_4^{2-}$  reduction, can neutralize acidity and change ionic concentrations significantly in some lakes (Kelly *et al.*, 1987; Mitchell *et al.*, 2001). Similar biological processes also occur in streams, and these processes have been demonstrated in Catskill streams (Burns, 1998). Nonetheless, to minimize the likely role of biological processes in lake chemistry, only drainage lakes were chosen that have a retention time of  $< 6$  months. This selection process yielded 12 lakes for analysis. Adequate stage data to allow flow estimation from the outlets of these lakes were unavailable. Some characteristics of these lakes and the Catskill streams are shown in Table II.

Samples for the ALTM lakes were collected monthly at the lake outlet in polyethylene bottles. Temperature was measured in the field, and samples were then transported on ice to the ALSC laboratory in Ray Brook, New York. The analytical procedures used are generally standard methods, and include pH potentiometrically with a glass electrode,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  by ion chromatography, base cations ( $\text{C}_B$ :  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) by atomic absorption spectrophotometer (AAS), ammonium ( $\text{NH}_4^+$ ) colorimetrically, and ANC by Gran

Table II. Physical characteristics of Adirondack lakes and Catskill streams analysed in this study

Surface Water	Drainage area (ha)	Elevation (m)	Location (N, W)	Retention time (years)
<i>Adirondacks</i>				
Arbutus Lake	365	513	43°58', 74°14'	0.48
Bubb Lake	186	553	43°46', 74°50'	0.27
Constable Pond	945	582	43°49', 74°48'	0.06
Dart Lake	10 756	536	43°47', 74°52'	0.05
Long Pond	26	570	43°50', 74°28'	0.17
Otter Lake Outlet	361	488	43°10', 74°30'	0.13
Owen Pond	1139	515	44°19', 73°54'	0.03
Lake Rondaxe	14 283	524	43°45', 74°54'	0.02
Sagamore Lake	4946	580	43°45', 74°37'	0.20
Squash Pond	41	648	43°49', 74°53'	0.14
West Pond	108	585	43°48', 74°53'	0.19
Windfall Pond	44	601	43°48', 74°49'	0.23
<i>Catskills</i>				
Biscuit Brook	959	630	42°00', 74°30'	—
East Branch Neversink River at Tison	2352	653	41°58', 74°27'	—
Neversink River at Claryville	17 247	471	41°53', 74°35'	—
Rondout Creek	1420	580	41°56', 74°23'	—
West Branch Neversink River at Winnisook	213	819	42°00', 74°25'	—

titration with strong acid. Monomeric aluminium was analysed during 1992–93 by complexation with 8-hydroxyquinoline, extraction into methyl isobutyl ketone, and analysis by AAS (Driscoll, 1984), and was modified in November 1993 to complexation by pyrocatechol violet and analysis in an automated spectrophotometer procedure (ALSC, 1993). The pyrocatechol violet method yields comparable results to that of the 8-hydroxyquinoline method (McAvoy *et al.*, 1992). Inorganic monomeric aluminium is determined as the difference between total monomeric and non-labile aluminium. Additional details of the analytical methods are provided in Driscoll and Van Dreaseon (1993; Driscoll *et al.*, 1998). Details of QA methods are provided in Schecher and Driscoll (1988) and USEPA (1991).

The Catskill streams were sampled at varying time intervals. Biscuit Brook was sampled weekly and during 6–12 storm and snowmelt events each year by an automated sampler. The West Branch Neversink River at Winnisook and East Branch Neversink River at Tison were sampled weekly during the early part of the record (1992–93), then monthly thereafter, and during 6–12 storm and snowmelt events each year. The Rondout Creek and Neversink River at Claryville were generally sampled monthly and during 6–12 storm and snowmelt events each year. These data sets of varying sample collection frequencies were converted into a monthly data set to enhance comparability with the ALTM data by eliminating the storm event samples and including only the samples collected manually closest to the 1st of each month.

Catskill samples were collected manually in 500 ml polyethylene bottles and kept on ice until they were transferred to a refrigerator at 4 °C in the laboratory. Sub-samples for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and ANC analysis were passed through 0.4  $\mu\text{m}$  polycarbonate filters prior to analysis, whereas sub-samples for analysis of  $\text{C}_\text{B}$  and aluminium fractions were not filtered.  $\text{C}_\text{B}$  sub-samples were acidified to  $\text{pH} < 1$  with HCl and shelf-stored, whereas all other sub-samples were refrigerated until analysis. Samples were analysed by similar methods to those of the Adirondack samples with two exceptions: (1)  $\text{C}_\text{B}$  analysis was by AAS until 1995 and by inductively coupled plasma emission spectroscopy thereafter; (2) monomeric aluminium was analysed by complexation with pyrocatechol violet and analysis in an automated spectrophotometer procedure. Details of analytical methods and QA/quality control procedures used at the US Geological Survey laboratory in Troy, New York, are provided in Lawrence *et al.* (1995) and Lincoln *et al.* (1996).

### Data analysis

Trend analysis was performed using the seasonal Kendall test (Hirsch *et al.*, 1982), a modification of the nonparametric Mann–Kendall test (Mann, 1945; Kendall, 1975). This test is useful for analysing monotonic trends in water quality data, which are commonly non-normally distributed, and contain outliers, missing values, and censored data (Hirsch *et al.*, 1982). Months were chosen as the seasons, and the trend test was applied to the residuals of a flow–concentration model developed for each constituent using either a hyperbolic (Johnson *et al.*, 1969) or natural log regression fit. In this manner, the effects of flow-related climate variability were reduced. Results of a trend test and flow–concentration model were considered statistically significant if  $p \leq 0.05$ . Acid-precipitation-related constituents that were analysed for trends and coherence included  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{H}^+$ , sum  $\text{C}_B$  ( $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ ), and  $\text{NH}_4^+$  in precipitation. Surface waters were analysed for the same constituents and additionally ANC.  $\text{NH}_4^+$  concentration trends were only evaluated in precipitation, because half or more of the measurements in many surface waters were below reporting limits of  $1\text{--}2 \mu\text{mol l}^{-1}$ .

Flow data for trend analysis were obtained from sites operated by the US Geological Survey using standard stream gauging methods (Rantz *et al.*, 1982). Stream gauges were operated at each of the five Catskill stream sites throughout the study period. However, neither lake level nor lake outlet stream-flow data were available for the Adirondack lakes (with one exception at the Arbutus Lake outlet, but not for the entire study period). Instead, flow data from the Independence River at Donnattsburg, New York (Figure 1), were related to concentration at each lake outlet. The Independence River drains a 22 973 ha watershed just west of the boundary of Adirondack Park, which includes numerous lakes and small ponds. Lawrence *et al.* (2004) found flow at this site to be broadly representative of hydrologic conditions in the western Adirondacks, where 10 of the 12 lakes included in this analysis are located.

Spatial coherence of temporal trends was examined by calculating the Pearson product-moment correlation for the 10 years of data for each pair of precipitation sites, surface water sites, and precipitation–surface water sites (Magnuson *et al.*, 1990; Baron and Caine, 2000). The mean correlation coefficient  $\rho$  was calculated for each pairwise comparison of each variable examined. Mean values of  $\rho$  within and among the two study regions were then used to determine coherence. A Bonferroni correction was applied to each  $\rho$  value, and a one-tailed test of significance was performed at the  $\alpha = 0.05$  level. With 10 years of data the  $\alpha = 0.05$  critical value of  $\rho = 0.602$ .

## RESULTS

### Precipitation chemistry

The slopes of significant trend lines for all six precipitation sites are shown in Table III for two time periods: (1) 1984–2001, and (2) 1992–2001. The 1992–2001 data represent the maximum length of record for all surface water sites, and the 1984–2001 data represent the maximum length of record for all precipitation sites, and are presented here because changes in surface water chemistry may be a response to changes in precipitation chemistry that predate the surface water record.

Trends of all ionic constituents analysed were generally similar between these two regions during 1984–2001.  $\text{SO}_4^{2-}$ ,  $\text{C}_B$ , and  $\text{H}^+$  concentrations decreased significantly at all six sites (Table III). The decreases in  $\text{SO}_4^{2-}$  concentrations were similar among the two regions, ranging from 1 to  $1.4 \mu\text{eq l}^{-1} \text{ year}^{-1}$ , and were approximately balanced by decreases in  $\text{H}^+$  concentrations.  $\text{NO}_3^-$  concentrations decreased significantly at five of six sites; these decreases were generally about one-third those of  $\text{SO}_4^{2-}$ , and were also similar among the regions. Trends in  $\text{NH}_4^+$  concentrations were generally not statistically significant; only the West Point site near the Catskills had a significant trend ( $+0.18 \mu\text{eq l}^{-1} \text{ year}^{-1}$ ).

Table III. Slope of trends ( $\mu\text{eq l}^{-1} \text{ year}^{-1}$ ) in precipitation chemistry at six NADP sites located near the study regions in the Adirondack and Catskill Mountains<sup>a</sup>

Site	1984–2001				1992–2001			
	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{H}^+$	$\text{C}_B$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{H}^+$	$\text{C}_B$
<i>Adirondacks</i>								
Bennett Bridge	–1.36	–0.43	–1.50	–0.17	NS	NS	NS	NS
Huntington Wildlife	–1.00	–0.30	–0.90	–0.19	NS	NS	–1.00	NS
Whiteface Mountain	–1.16	–0.19	–0.86	–0.14	–0.94	NS	–0.80	NS
<i>Catskills</i>								
Biscuit Brook	–1.04	NS	–0.95	–0.19	NS	NS	NS	NS
Milford	–1.15	–0.34	–1.29	–0.25	NS	NS	–0.92	NS
West Point	–1.16	–0.40	–1.35	–0.20	–1.08	NS	–1.16	NS

<sup>a</sup> NS: not significant,  $p > 0.05$ .

There were fewer significant trends during 1992–2001 than during 1984–2001 (Table III). Only two sites showed significant decreases in  $\text{SO}_4^{2-}$  concentrations, and these decreases were similar to those at the same sites during 1984–2001, about  $1 \mu\text{eq l}^{-1} \text{ year}^{-1}$ . Four of six sites showed significant decreases in  $\text{H}^+$  concentrations during 1992–2001; two of these sites also showed significantly decreasing  $\text{SO}_4^{2-}$  concentrations. There were no significant trends in  $\text{NO}_3^-$ ,  $\text{C}_B$  (Table III), or  $\text{NH}_4^+$  (data not shown) concentrations during 1992–2001.

The annual mean concentrations generally indicate high and statistically significant temporal coherence among the three NADP sites in the Catskills (Figure 2). Comparisons among the three Adirondack NADP sites and the six inter-regional NADP sites indicate generally less temporal coherence than among the Catskill NADP sites. Only  $\text{SO}_4^{2-}$  and  $\text{H}^+$  are significantly coherent in the Adirondack and inter-regional comparisons, and the mean  $\rho$  values are less than those for the Catskill sites.  $\text{NO}_3^-$  showed the weakest temporal coherence among the chemical constituents examined for both comparisons.

#### Surface water chemistry

Many significant flow-weighted trends were evident in the data from Catskill streams and Adirondack lakes (Table IV, Figure 3). Decreasing trends in  $\text{SO}_4^{2-}$  concentrations were evident for all Catskill streams

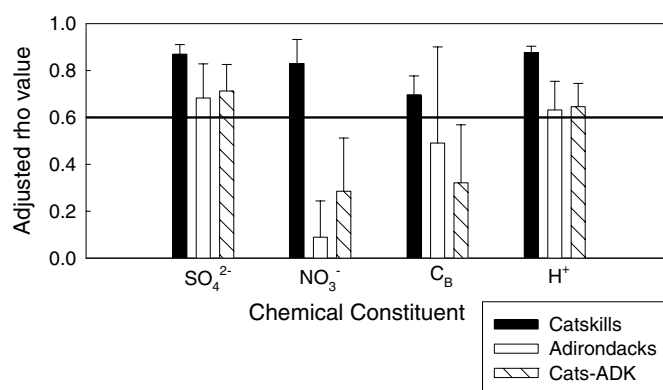


Figure 2. Mean regional and cross-regional temporal coherence of precipitation chemistry during 1992–2001 at six NADP sites near the Catskill and Adirondack Mountains as indicated by the mean  $\rho$  value based on three correlations in each of the regions and six cross-regional correlations. Error bars indicate standard deviation of the mean and are only shown above the mean value but are inferred to extend below as well. Black horizontal line is the  $\rho$  value of 0.602 at which the relation is significant at  $p = 0.05$

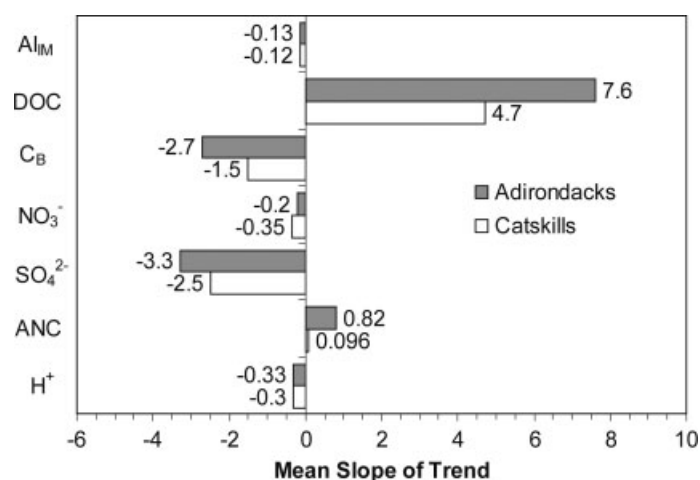


Figure 3. Mean flow-corrected trend during 1992–2001 at five Catskills streams and 12 Adirondack lakes. Trends for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , ANC,  $\text{C}_B$ , and  $\text{H}^+$  are in units of  $\mu\text{eq l}^{-1} \text{ year}^{-1}$ . Trends for inorganic monomeric aluminium ( $\text{Al}_{\text{IM}}$ ) and dissolved organic carbon (DOC) are in units of  $\mu\text{mol l}^{-1} \text{ year}^{-1}$ . Trends that were not statistically significant were counted as a trend of zero when calculating mean values

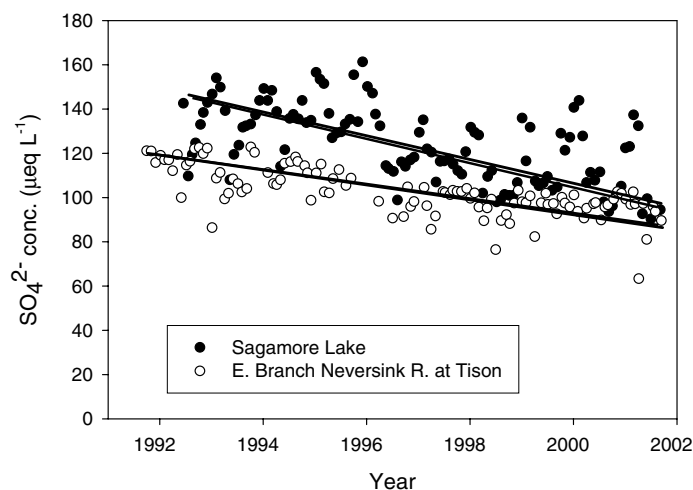


Figure 4. Monthly  $\text{SO}_4^{2-}$  concentrations at Sagamore Lake in the Adirondacks and at East Branch Neversink River at Tison in the Catskills during 1992–2001. The solid black lines represent the seasonal Kendall trend slope fit through each data set

and Adirondack lakes, and the mean values of those trends were  $-2.5 \mu\text{eq l}^{-1} \text{ year}^{-1}$  in the Catskills and  $-3.3 \mu\text{eq l}^{-1} \text{ year}^{-1}$  in the Adirondacks. Representative monthly  $\text{SO}_4^{2-}$  concentrations are shown for Sagamore Lake in the Adirondacks and the East Branch Neversink River at Tison (Figure 4). These sites are shown because they represent the median values of variance observed in each data set. The  $\text{SO}_4^{2-}$  concentrations from the East Branch Neversink River at Tison show less scatter about the trend line than the  $\text{SO}_4^{2-}$  concentrations from Sagamore Lake do, typical of the differences observed between these Catskill and Adirondack data.

Smaller decreasing trends in  $\text{NO}_3^-$  concentrations were found at 60% of Catskill streams and 50% of Adirondack lakes (one lake had a significant increasing trend), and the mean values of those trends were  $-0.35 \mu\text{eq l}^{-1} \text{ year}^{-1}$  in the Catskills and  $-0.2 \mu\text{eq l}^{-1} \text{ year}^{-1}$  in the Adirondacks.



Table IV. Flow-corrected (FC) and non-flow-corrected (NFC) trends ( $\mu\text{eq l}^{-1} \text{ year}^{-1}$ ) at five Catskill streams and 12 Adirondack lakes during 1992–2001. The bold trend was selected to represent these data (selection process explained in text)

Site	$\text{SO}_4^{2-}$		$\text{NO}_3^-$		ANC		$\text{C}_\text{B}$	
	FC	NFC	FC	NFC	FC	NFC	FC	NFC
<i>Adirondacks</i>								
Arbutus Lake	-2.37	<b>-2.50</b>	NS	NS	NS	NS	<b>-3.27</b>	<b>-3.28</b>
Bubb Lake	-3.12	<b>-3.21</b>	<b>-0.36</b>	-0.55	<b>1.92</b>	2.43	<b>-2.27</b>	<b>-1.94</b>
Constable Pond	-3.63	<b>-3.61</b>	NS	-0.57	<b>1.43</b>	1.69	<b>-2.60</b>	<b>-1.94</b>
Dart Lake	-3.21	<b>-3.21</b>	<b>-0.85</b>	-0.92	<b>1.52</b>	1.68	-2.10	-2.10
Long Pond	-3.56	<b>-3.61</b>	NS	NS	1.21	1.52	-1.90	<b>-1.87</b>
Otter Lake Outlet	-2.41	<b>-2.53</b>	NS	-0.30	<b>1.44</b>	1.57	<b>-0.80</b>	NS
Owen Pond	-4.64	<b>-4.46</b>	<b>0.89</b>	0.62	NS	2.14	<b>-3.06</b>	<b>-2.72</b>
Lake Rondaxe	<b>-2.67</b>	-2.78	<b>-0.74</b>	-0.94	1.35	1.34	-2.67	<b>-2.10</b>
Sagamore Lake	-3.96	<b>-4.06</b>	<b>-0.94</b>	-1.15	NS	NS	-4.42	<b>-4.08</b>
Squash Pond	-2.75	<b>-2.71</b>	NS	NS	<b>1.03</b>	1.01	-1.71	-1.69
West Pond	<b>-3.26</b>	-3.61	<b>-0.35</b>	-0.48	NS	NS	-4.16	-4.13
Windfall Pond	-3.57	<b>-3.72</b>	NS	-0.47	NS	1.87	-3.68	<b>-2.23</b>
<i>Catskills</i>								
Biscuit Brook	<b>-3.60</b>	-3.35	<b>-0.44</b>	-0.58	<b>0.48</b>	0.85	-2.67	<b>-2.27</b>
East Branch Neversink River at Tison	<b>-2.31</b>	-2.43	<b>-0.65</b>	-0.59	NS	NS	<b>-1.94</b>	<b>-1.83</b>
Neversink River at Claryville	-2.12	<b>-2.10</b>	NS	NS	NS	NS	NS	NS
Rondout Creek	<b>-2.40</b>	-2.55	NS	NS	NS	0.45	-2.19	<b>-1.67</b>
West Branch Neversink River at Winnisook	-2.30	-2.29	-0.66	<b>-0.74</b>	NS	<b>0.45</b>	-0.82	<b>-1.28</b>

NS: not significant,  $p > 0.05$ .

Decreasing trends in acid anion concentrations were accompanied by similar trends in  $\text{C}_\text{B}$ ; Catskill streams decreased by a mean of  $-1.5 \mu\text{eq l}^{-1} \text{ year}^{-1}$  (significant decreases at 80% of sites) and Adirondack lakes decreased by a mean of  $-2.7 \mu\text{eq l}^{-1} \text{ year}^{-1}$  (significant decreases at all sites). Additionally, mean decreasing trends in inorganic monomeric aluminium concentrations of  $-0.12 \mu\text{mol l}^{-1} \text{ year}^{-1}$  and  $-0.13 \mu\text{mol l}^{-1} \text{ year}^{-1}$  were noted for the Catskill streams and Adirondack lakes respectively.

Increasing trends were noted in several constituents (Table IV, Figure 3). ANC increased by a mean of  $0.82 \mu\text{eq l}^{-1} \text{ year}^{-1}$  in the Adirondack lakes (significant increases at 58% of sites), whereas only Biscuit Brook in the Catskills showed an increasing trend in ANC. The other four Catskill streams, however, had increasing trends of ANC that were of marginal statistical significance ( $0.1 > p > 0.05$ ). Additionally,  $\text{H}^+$  concentrations decreased significantly at 20% of Catskill streams and 75% of Adirondack lakes (one lake had a significant increasing trend); the mean  $\text{H}^+$  decrease was  $0.3 \mu\text{eq l}^{-1} \text{ year}^{-1}$  in the Catskill streams and  $0.33 \mu\text{eq l}^{-1} \text{ year}^{-1}$  in the Adirondack lakes. Finally, increasing trends in DOC concentrations were evident at 80% of Catskill streams (mean carbon:  $4.7 \mu\text{mol l}^{-1} \text{ year}^{-1}$ ) and 75% of Adirondack lakes (mean carbon:  $7.6 \mu\text{mol l}^{-1} \text{ year}^{-1}$ ).

Trends in surface water chemistry showed high temporal coherence for  $\text{SO}_4^{2-}$  concentrations, but generally weak and statistically insignificant coherence for the other constituents (Figure 5). Temporal coherence of  $\text{SO}_4^{2-}$  concentrations as measured by the mean  $\rho$  value was  $>0.9$  for the Catskill streams, about 0.7 for the Adirondack lakes, and about 0.7 for the inter-regional comparison of surface waters. The mean  $\rho$  value for temporal coherence was also statistically significant for  $\text{C}_\text{B}$  concentrations among the Adirondack lakes, and was just below the significance threshold for  $\text{C}_\text{B}$  and  $\text{NO}_3^-$  concentrations among the Catskill streams. All other mean  $\rho$  values were  $<0.5$ , reflecting weak trend coherence.

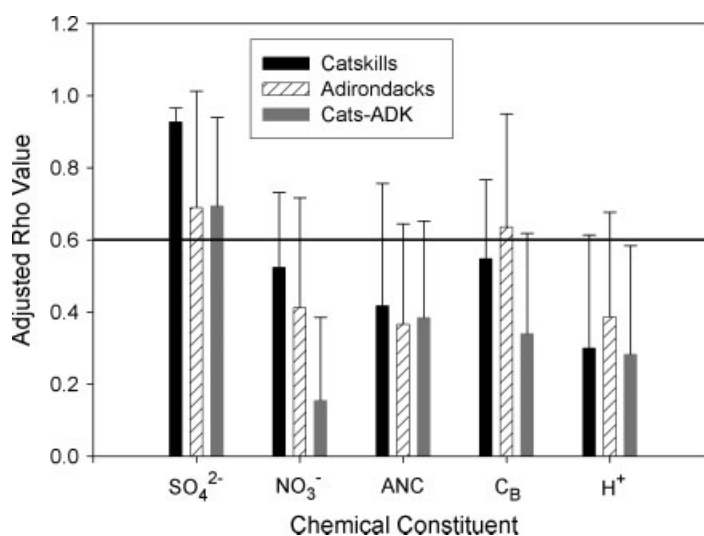


Figure 5. Regional and cross-regional temporal coherence of surface water chemistry during 1992–2001 at five Catskill streams and 12 Adirondack lakes as indicated by the mean  $\rho$  value based on 10 correlations among the Catskill streams, 66 correlations among the Adirondack lakes, and 60 correlations among the cross-regional surface waters. Error bars indicate standard deviation of the mean and are only shown above the mean value but are inferred to extend below as well. Black horizontal line is the  $\rho$  value of 0.602 at which the relation is significant at  $p = 0.05$

*Comparison of flow-corrected and non-flow-corrected trends.* Correcting for flow effects did not change the direction of any trend determined without flow correction; however, flow correction did change the statistical significance of some trends (Table IV). For example, three Adirondack lakes have non-significant flow-corrected trends in  $\text{NO}_3^-$  concentrations that are significant decreasing trends in the absence of flow correction. Additionally, four non-significant flow-corrected trends in ANC at Adirondack lakes and Catskill streams would otherwise be significant in the absence of flow correction. The effects of flow correction did not change the significance status of any  $\text{SO}_4^{2-}$  trend and changed the significance status of only one  $\text{C}_B$  trend. Overall, the mean regional trends for both of these constituents changed little with flow correction.

*Temporal coherence of precipitation and surface water chemistry.* Strong temporal coherence of trends was found among precipitation sites and surface waters for  $\text{SO}_4^{2-}$  concentrations in the Catskills, where the mean  $\rho$  value was  $>0.75$  (Figure 6). Additionally, the coherence of precipitation–surface water trends was of borderline statistical significance for  $\text{SO}_4^{2-}$  concentrations in the Adirondacks. However, the temporal coherence of trends in  $\text{NO}_3^-$ ,  $\text{C}_B$ , and  $\text{H}^+$  concentrations was weak (mean  $\rho < 0.2$ ) in both regions.

## DISCUSSION

### *Precipitation chemistry*

Decreasing trends in  $\text{SO}_4^{2-}$  concentrations in precipitation in the northeastern USA in the 1980s and 1990s are paralleled by decreases in  $\text{SO}_2$  emissions in the Ohio River Valley, and have been attributed in part to emissions limits established under Title IV of the 1990 *Clean Air Act Amendments* (Stoddard *et al.*, 1999; Lynch *et al.*, 2000). The decreasing trends in precipitation  $\text{SO}_4^{2-}$  concentrations observed during 1984–2001 were similar to those reported in recent studies that included many or all of the same sites in New York, but extended over slightly different time periods (1981–98: Nilles and Conley, 2001; 1978–2000: Driscoll *et al.*, 2003), but less than those reported for earlier periods in the early 1980s to the mid-1990s (Shannon, 1999; Lynch *et al.*, 2000). Additionally, a recent study reported a median decrease in precipitation  $\text{SO}_4^{2-}$

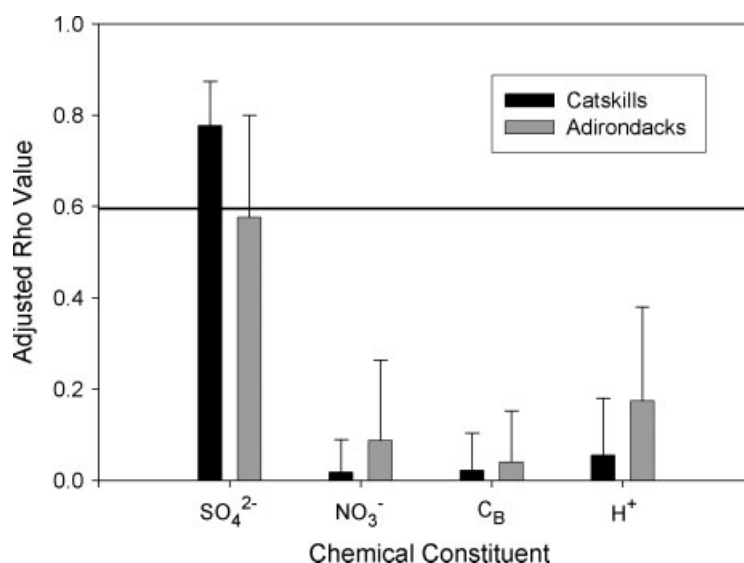


Figure 6. Regional temporal coherence of precipitation and surface water chemistry during 1992–2001 among three NADP sites and five streams in the Catskills and three NADP sites and 12 lakes in the Adirondacks as indicated by the mean  $\rho$  value based on 15 correlations among the Catskill sites and 36 correlations among the Adirondack sites. Error bars indicate the standard deviation of the mean and are only shown above the mean value but are inferred to extend below as well. Black horizontal line is the  $\rho$  value of 0.602 at which the relation is significant at  $p = 0.05$

concentrations of  $0.8$  to  $1.5 \mu\text{eq l}^{-1} \text{ year}^{-1}$  from 1990–2000 across five acid-sensitive regions of the eastern USA (Kahl *et al.*, 2004), whereas the present study finds a similar decrease at only 33% of the sites examined in New York over the period 1992–2001. The reason for this difference is unclear. Together, however, these numerous trend observations are broadly consistent with  $\text{SO}_2$  emissions from Title-IV-affected units (primarily power plants in the Ohio River Valley) that showed a sharp decrease of about 25% from 1994 to 1995 (when Title IV limits went into effect) and only a modest decrease of about 10% from 1995 to 2001 ([www.epa.gov/airmarkets/emissions](http://www.epa.gov/airmarkets/emissions)). These trends are qualitatively consistent with temporal patterns in annual mean volume-weighted  $\text{SO}_4^{2-}$  concentrations at the six NADP sites analysed in this study in which the years with the highest  $\text{SO}_4^{2-}$  concentrations generally occurred before 1995, and the trends flatten thereafter (Figure 7).

The downward trends in  $\text{NO}_3^-$  concentrations in atmospheric deposition reported here are similar to those reported in two previous studies in New York or the northeastern USA (Driscoll *et al.*, 2003; Kahl *et al.*, 2004). These trends are less than those of  $\text{SO}_4^{2-}$ ; however, they are broadly consistent with decreases in Title-IV-affected  $\text{NO}_x$  emissions (which are only one-third of total  $\text{NO}_x$  emissions) of nearly 30% from 1990–2001 ([www.epa.gov/airmarkets/emissions](http://www.epa.gov/airmarkets/emissions)). However, about half of atmospheric N deposition is believed to originate from vehicle emissions, which are not regulated under Title IV, and, furthermore, should yield more local influence on N deposition patterns; therefore,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  trends in wet deposition are not expected to be identical.

The high temporal coherence of mean annual  $\text{SO}_4^{2-}$  concentrations at NADP sites near the Catskills and Adirondacks and in the inter-regional comparison suggests that precipitation  $\text{SO}_4^{2-}$  chemistry primarily reflects broad regional patterns in emissions and atmospheric transport and transformation processes. In contrast,  $\text{NO}_3^-$  trends were coherent only at the Catskill sites, suggesting that local-scale variations in sources and atmospheric transport and transformation processes influence  $\text{NO}_3^-$  chemistry in the Adirondacks and across both regions. This suggests that future temporal trends in precipitation  $\text{NO}_3^-$  chemistry may show some divergence within the Adirondacks and across the Adirondacks and Catskills.

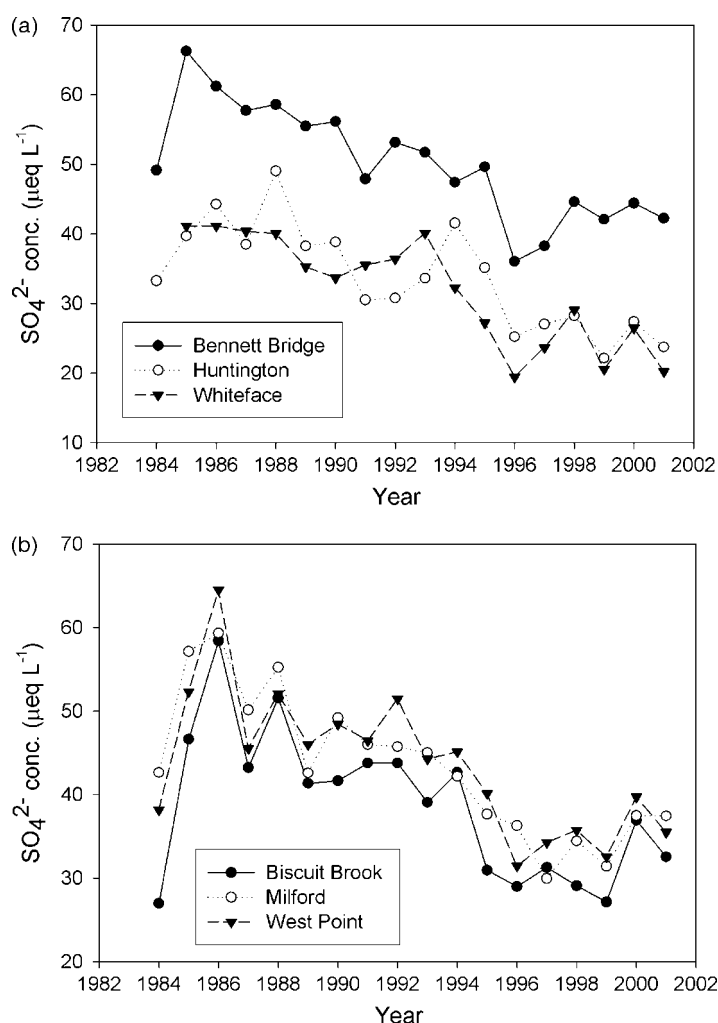


Figure 7. Annual mean volume-weighted  $\text{SO}_4^{2-}$  concentrations at the six NADP sites that were analysed in this study: (a) Adirondacks sites; (b) Catskill sites

#### Surface water chemistry

**$\text{SO}_4^{2-}$  concentrations.** Decreasing trends in surface water  $\text{SO}_4^{2-}$  concentrations were the largest and most widespread of those found in this study. These  $\text{SO}_4^{2-}$  concentration trends generally showed high synchronicity within each region (though somewhat higher in the Catskills) and among the two regions. Similarly, precipitation–surface water  $\text{SO}_4^{2-}$  concentration trends showed moderate (Adirondacks lakes) to high (Catskill streams) temporal coherence. Despite high temporal coherence of surface water  $\text{SO}_4^{2-}$  trends, however, two-thirds of 1992–2001 trends in volume-weighted precipitation  $\text{SO}_4^{2-}$  concentrations at six NADP sites near both regions were not significant. These results suggest two possibilities: (1) there are lags in these ecosystems, such that surface water trends during 1992–2001 may be responding to longer term changes in precipitation  $\text{SO}_4^{2-}$  concentrations; (2) surface water trends are responding in part to changes in dry deposition of sulphur (S), which are not reflected in NADP data. Decreases in precipitation  $\text{SO}_4^{2-}$  concentrations are more pronounced and are statistically significant at all six NADP sites during 1984–2001, which supports the first hypothesis above; however, these  $\text{SO}_4^{2-}$  trends are only about one-half to one-third

as large as the surface water  $\text{SO}_4^{2-}$  trends. Steeper trends in surface waters than precipitation are expected because evapotranspiration alone (in the absence of other biogeochemical processes) would be expected to concentrate solutes by as much as 100%, which could result in a doubling of surface water trends relative to precipitation trends. Since many of the trends in precipitation  $\text{SO}_4^{2-}$  concentrations are less than half those of surface waters, these ecosystems are also likely either 'bleeding out' excess stored  $\text{SO}_4^{2-}$  or are experiencing trends in dry deposition of S that exceed those of trends in  $\text{SO}_4^{2-}$  concentration in wet deposition. If the dry deposition hypothesis is correct, then the Catskill streams would be expected to show greater decreases in  $\text{SO}_4^{2-}$  concentrations than the Adirondack lakes, because the Catskills are closer to large metropolitan source areas of dry deposition, such as New York City and Philadelphia. These data show just the opposite: the mean  $\text{SO}_4^{2-}$  trend in the Adirondack lakes was  $-3.3 \mu\text{eq l}^{-1} \text{ year}^{-1}$  and the mean  $\text{SO}_4^{2-}$  trend in the Catskill streams was  $-2.5 \mu\text{eq l}^{-1} \text{ year}^{-1}$ . Resolution of these hypotheses will require additional analysis of the temporal dynamics of S pools in these ecosystems and analysis of temporal trends in the dry deposition of S.

**$\text{C}_\text{B}$  concentrations.** Decreasing trends in  $\text{C}_\text{B}$  concentrations were almost as prevalent (88% of trends examined were significant) and of slightly lower magnitude than those of  $\text{SO}_4^{2-}$  concentrations in these surface waters. As with  $\text{SO}_4^{2-}$  trends, decreasing  $\text{C}_\text{B}$  trends were of lower magnitude in the Catskill streams than in the Adirondack lakes. This lower decrease in  $\text{C}_\text{B}$  concentrations explains in part why ANC is increasing in most of these surface waters. These results contrast with those of previous trend studies in the Catskills and Adirondacks that extended through the mid-1990s, in which decreases in  $\text{C}_\text{B}$  concentrations exceeded those of  $\text{SO}_4^{2-}$  concentrations, resulting in no increase in ANC (Burns *et al.*, 1998; Driscoll *et al.*, 1998; Stoddard *et al.*, 1999). More-recent trend analysis results from these and nearby regions concur that decreasing  $\text{SO}_4^{2-}$  trends now exceed those of  $\text{C}_\text{B}$ ; therefore, widespread increases in surface water ANC in the northeastern USA have become evident (Driscoll *et al.*, 2003; Kahl *et al.*, 2004).

**$\text{NO}_3^-$  concentrations and ANC.** The dominant pattern in surface water trends in these two regions was decreases in  $\text{NO}_3^-$  concentrations and increases in ANC. This pattern, however, was not as prevalent for ANC as for  $\text{NO}_3^-$ , and  $\text{NO}_3^-$  trends were less prevalent than those of  $\text{SO}_4^{2-}$  and  $\text{C}_\text{B}$ . For example, only 58% of Adirondack lakes and 60% of Catskill streams had significant trends in  $\text{NO}_3^-$  concentrations. Additionally, both  $\text{NO}_3^-$  and ANC had the greatest number of trends (seven in total) that were significant without flow correction and not significant with flow correction prior to trend analysis.  $\text{NO}_3^-$  concentrations and ANC are typically strongly related to flow in Catskill streams and Adirondack lake outlets (Murdoch and Stoddard, 1993; Mitchell *et al.*, 2001).  $\text{NO}_3^-$  concentrations generally increase with flow and ANC decreases with flow, and the most extreme values are often measured during spring snowmelt (Driscoll *et al.*, 1987; Murdoch and Stoddard, 1992). Flow sensitivity of chemical constituents can affect trends when climate conditions differ at the beginning and end of the record. In the case of the Adirondack lakes with  $\text{NO}_3^-$  concentration trends that were significant without flow correction but not significant with flow correction, this may indicate generally drier climatic conditions with lower flow and lower  $\text{NO}_3^-$  concentrations at the end of the record. An examination of data from Independence River that was used as an index site for the Adirondack lakes indicates that mean annual flow was lower by 12.5% during water years 1999–2001 at the end of the record than during water years 1992–94 at the beginning of the record, confirming generally drier conditions at the end of the record. The distinction between flow-corrected and non-flow-corrected trends is important, because flow correction accounts for some aspects of climate variability and, therefore, allows a more direct examination of the effects of changes in precipitation chemistry on surface water chemistry trends. The results of this study indicate that flow correction is important when assessing trends in flow-sensitive chemical constituents like  $\text{NO}_3^-$  and ANC, but less important for constituents like  $\text{SO}_4^{2-}$ , which is less flow sensitive. Lawrence *et al.* (2004) also found that trends in pH and ANC in Adirondack streams were strongly affected by flow conditions and concluded that such trends could not be directly related to changes in the acidity of precipitation.

**DOC concentrations.** One of the surprising results of this study was the prevailing presence of increasing trends in DOC concentrations. These trends averaged  $7.6 \mu\text{mol l}^{-1} \text{ year}^{-1}$  in the Adirondack lakes (significant at 75% of sites) and  $4.7 \mu\text{mol l}^{-1} \text{ year}^{-1}$  in the Catskill streams (significant at 80% of sites). A similar increasing trend in DOC concentrations was recently noted at a small percentage of ALTM lakes (Driscoll *et al.*, 2003), of which the current study examined a subset, but here the trends are more prevalent. These increasing trends, however, contrast with decreasing trends recently reported for several lakes in Ontario, Canada (Gunn *et al.*, 2001). Trends in DOC are important for several reasons:

1. DOC concentration changes can affect surface water pH and ANC and can, in turn, be affected by changes in pH and ANC (Kullberg *et al.*, 1993).
2. DOC affects water colour and light penetration; thus, changes in DOC concentrations can change aquatic productivity and affect the aquatic food web and lake stratification (Keller *et al.*, 2003).
3. DOC concentration changes may reflect aspects of climate change, such as increasing air temperature, decreasing snowmelt, and decreasing solar radiation (Freeman *et al.*, 2001; Hudson *et al.*, 2003).
4. DOC concentrations are related to the formation of carcinogenic disinfection by-products, such as trihalomethane (Stevens *et al.*, 1976).

This last item is important, because all of the Catskill streams studied here flow into reservoirs that provide a water supply to New York City, which does not treat or filter the water to remove DOC. Increases in surface water DOC concentrations coupled with increases in pH may also decrease inorganic monomeric aluminium and increase organic monomeric aluminium, which should decrease fish toxicity in these waters (Driscoll *et al.*, 2003). Finally, DOC concentrations in surface waters are often strongly related to those of dissolved organic nitrogen (DON), and since DON may replace  $\text{NO}_3^-$  as the principal exported form of N as  $\text{NO}_3^-$  concentrations decrease (Perakis and Hedin, 2002), an increasing trend in DOC concentrations may in part explain the decreasing trend in  $\text{NO}_3^-$  concentrations that was observed in most of these surface waters. Presently, we are uncertain of the cause or causes of these increasing trends in DOC concentrations reported here; however, several hypotheses, such as the effects of pH on solubility and changes in air temperature and precipitation, provide possible explanations and should be explored in future research studies.

## CONCLUSIONS

The results of this study indicate that  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{C}_B$  concentrations have decreased, and pH has increased in precipitation during 1984–2001 at sites near the Catskill and Adirondack regions of New York State, whereas many fewer significant trends were found during the last 10 years of the record, indicating that most of the change occurred during 1984–91. Data from five Catskill streams and 12 short-residence-time Adirondack lakes showed uniformly decreasing trends in  $\text{SO}_4^{2-}$  concentrations that generally averaged  $2.5\text{--}3.5 \mu\text{eq l}^{-1} \text{ year}^{-1}$ . This is more than twice the rate of decrease during 1984–2001 in precipitation  $\text{SO}_4^{2-}$  concentrations, suggesting that, in addition to the effects of evapotranspiration on trends, there is either a lag in response or a sharper decrease in dry deposition of S. Most surface waters in the two regions showed decreasing trends in  $\text{NO}_3^-$  and  $\text{C}_B$  concentrations and increasing trends in ANC and pH that were less than those of  $\text{SO}_4^{2-}$ . Most sites also showed increasing trends in DOC concentrations, caused by either decreasing surface water acidity or climate variation over the study period. These DOC trends are likely to be ecologically significant and may also be significant in the Catskills (from which New York City derives most of its water supply) because of the link between DOC and the formation of disinfection by-products.

Temporal coherence of trends in  $\text{SO}_4^{2-}$  concentrations was significant in both regions in precipitation, surface waters, and precipitation–surface water comparisons, indicating strong synchronicity among wet deposition and watershed S cycling processes. Temporal coherence for  $\text{NO}_3^-$  and  $\text{C}_B$  concentrations and

ANC was much weaker and generally non-significant, though a tendency towards higher synchronicity in the Catskills was noted. The lack of a strong temporal coherence in ANC indicates that local-scale processes and factors that affect the rates of cycling of N and C<sub>B</sub> are significant and are likely to confound a simple cause–effect relation between S and N emission trends and the response of acid–base conditions of surface waters in these two acid-sensitive regions.

#### ACKNOWLEDGEMENTS

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